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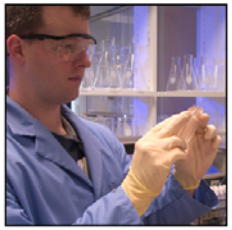
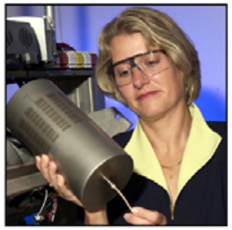
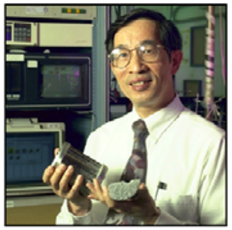
Ion Exchange and Adsorption Processes

David T. Hobbs


Introduction to Nuclear Chemistry and Fuel Cycle Separations

SRNL-STI-2009-00461

Topics

- Fundamentals
- Historical Perspectives
- Types of Ion Exchangers
- Industrial Applications
- Nuclear Fuel Cycle Applications
- Conclusions

Adsorption

- Adhesion of a gas, liquid or dissolved substance to a surface
- Commercial applications
  - Bulk gas separations/purification:
    N_2/O_2, paraffins, isoparaffins, aromatics, CO, CH_4, CO_2, NH_3/H_2
  - Bulk liquid separations/purification:
    paraffins, isoparaffins, aromatics, fructose/glucose
- Major classes of sorbents
  - Molecular-sieve zeolites
  - Activated alumina
  - Silica gel
  - Activated carbon

Ion Exchange

- Chemical process whereby ions are reversibly transferred between an insoluble solid and a fluid

- Cation Exchange: $S\text{-}H_{(s)} + Na^{+}_{(aq)} = S\text{-}Na_{(s)} + H^{+}_{(aq)}$

- Anion Exchange: $S\text{-}Cl_{(s)} + NO_3^{-}{}_{(aq)} = S\text{-}NO_{3(s)} + Cl^{-}_{(aq)}$

- Selectivity is function of ion valence & size, ionic form of resin, ionic strength of solution, type of functional group, nature of non-exchanging groups

Historical Perspectives – Ion Exchange

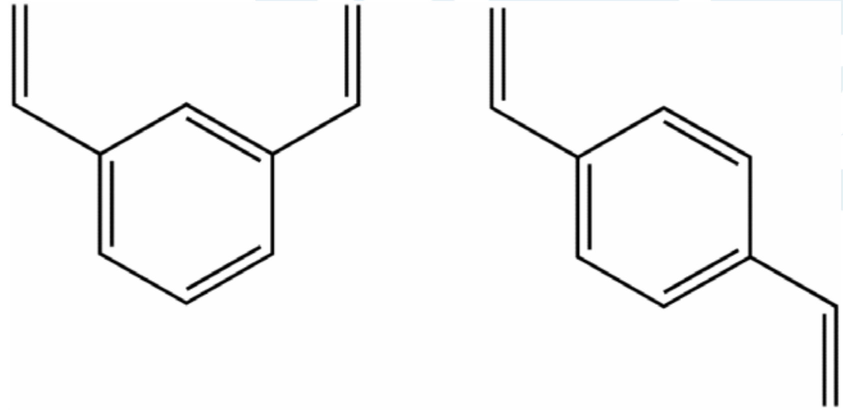
- Natural phenomena that occurs in soil, minerals and tissues of plants and animals
- Thompson and Way (1850) first described process in soils
- Eichorn (1858) demonstrated that process in reversible
- Gans (1905) developed first practical ion exchange process for softening water using sodium aluminates
- Adams and Holms (1935) developed first polymer derived ion exchangers

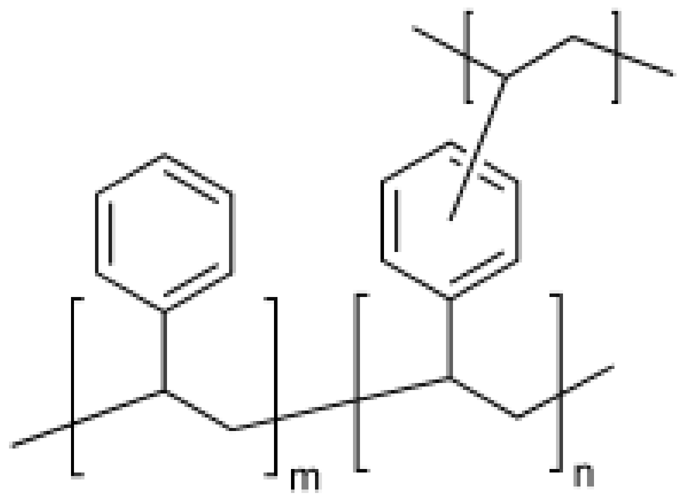
Historical Perspectives

- D'Alelio (1944) developed materials based on styrene divinylbenzene matrix

- Juda and McRae (1950) developed ion exchange products in form of membranes

- Grot (1970) develops Nafion® ion exchange membrane
  - chlor-alkali electrolyzers
  - PEM fuel cells

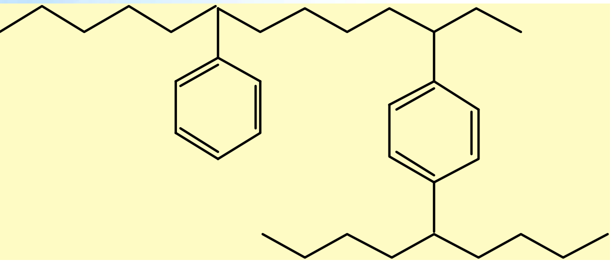




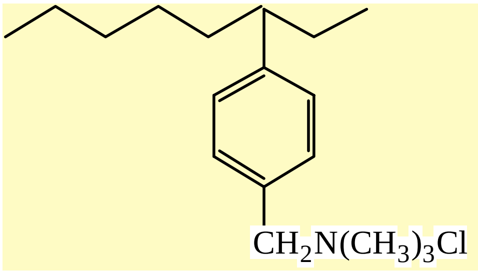
Historical Perspectives

- Lynch, Dosch, Kenna, Johnstone and Nowak (1975) report ion exchange behavior of titanates and zirconates
  - SRS uses monosodium titanate for Sr/actinide removal (1995)
- Dosch and Anthony (1992) report high affinity of crystalline silicotitanates (CST) for cesium under strongly alkaline conditions
- Bibler and Wallace (1995) patent resorcinol formaldehyde (RF) resin for cesium removal
- Tarbet, Maas, Krakowski and Bruening patent hydroxyarylene resin (SuperLiq® 644) for cesium removal

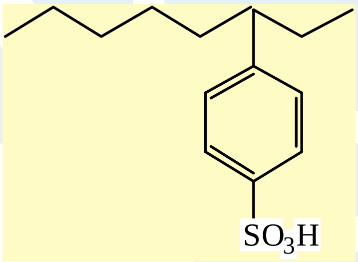
Types of Ion Exchangers - Organic



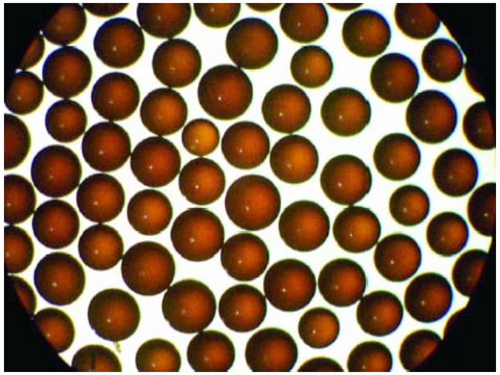
Polymer backbone



Anion exchange

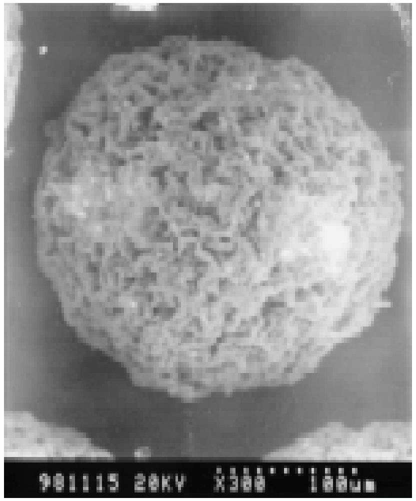


Cation exchange



Gel ion exchange resins are translucent and are a homogeneous continuous phase throughout the bead. The pore structure of gel resins depends on the degree of crosslinking.

Macroporous resins are opaque due to the fact that they contain up to 20% DVB in the polymer matrix. They are produced from a styrene-divinylbenzene copolymer to which has been added a non-polymerizable diluent that volatilizes leaving discrete macro pores throughout the bead.



Y. Yu, et. al, J. Chromatog. A, 1999 *985*, 129-136.

Types of Ion Exchangers - Inorganic

- Silicates
  - Aluminum silicates (zeolites)
  - Titanium silicates
- Hexacyanoferrates
  - $K_2MFe(CN)_6$, where M = Ni, Co, Cu
- Hydrous metal oxides
  - Sodium titanates & zirconates
  - Pentavalent metal oxides (Sb, Ta, Nb)
  - Mixed metal oxides ($A_2B_2O_7$)
- Metal phosphates (Zr, Ca, Mo)
- Group(IV) Acid Salts (Ti, Hf, Ge, Sn)

Type A

Type B

UOP molecular sieve products

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Physical & Chemical Properties

- Physical properties
  - density
  - resistance to osmotic shock
  - diffusion
  - relative porosity
- Chemical properties
  - hydration
  - ionization
  - selectivity

Industrial Applications – Water Treatment

- Cation Exchange
  - sodium cycle – softening
  - hydrogen cycle - dealkylization
- Anion Exchange
- Deionization
- Electric Power Generation
- Recovery of valuable metals
- Removal of toxic metals

Sodium Cycle - Softening

- Remove calcium & magnesium from natural water supplies
- Materials: zeolites, synthetic aluminosilicates & high-capacity polymer resins

Loading:

$$CaCO_3 + 2R\text{-}Na = R_2\text{-}Ca + Na_2CO_3$$

$$MgSO_4 + 2R\text{-}Na = R_2\text{-}Mg + Na_2SO_4$$

Regeneration:

$$2NaCl + R_2\text{-}Ca = 2R\text{-}Na + CaCl_2$$

$$2NaCl + R_2\text{-}Mg = 2R\text{-}Na + MgCl_2$$

Hydrogen Cycle - Dealkalization

- Removal of alkalinity from water supplies
- Materials: weak carboxylic acid (R-COOH) resins

Loading:

$$CaCO_3 + 2R\text{-}COOH = (R\text{-}COO)_2Ca + Na_2CO_3$$

$$NaHCO_3 + R\text{-}COOH = R\text{-}COONa + H_2CO_3$$

Regeneration:

$$(R\text{-}COO)_2Ca + H_2SO_4 = 2R\text{-}COOH + CaSO_4$$

$$(R\text{-}COONa + H_2SO_4 = 2R\text{-}COOH + Na_2SO_4$$

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Anion Exchange

- Remove toxic anions from water supplies
- Ion exchange materials: strong base anion exchangers

Loading:

$$R\text{-}Cl + NO_3^- = R\text{-}NO_3 + Cl^-$$

$$R\text{-}Cl + NO_2^- = R\text{-}NO_2 + Cl^-$$

$$2R\text{-}Cl + SO_4^{2-} = 2R\text{-}SO_4 + 2Cl^-$$

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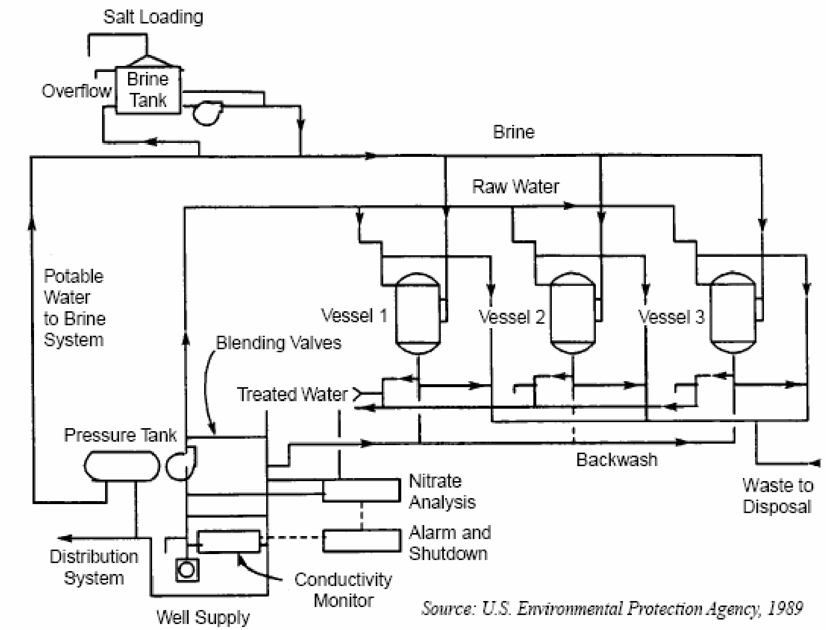
Deionization

- Remove all ions from water supplies
- Ion exchange materials: strong acid cation exchangers in series with weak base anion exchanger or strong base anion exchanger in the hydroxyl form



Source: U.S. Environmental Protection Agency, 1989

Loading:

$$R\text{-}SO_3H + MX = R\text{-}SO_3M + HX$$

$$R\text{-}N(CH_3)_2 + HX = R\text{-}N(CH_3)_2HX$$

$$R\text{-}N(CH_3)_3OH + HX = R\text{-}N(CH_3)_2X + H_2O$$

Electric Power Generation

- Remove dissolved solids in water fed to produce ultrapure water
  - supercritical boiler (fossil fuel)
  - pressurized water reactors
  - boiling water reactors
  - spent fuel cooling basins
- Mixed bed ion exchange systems in NH_4/OH or Li/OH form

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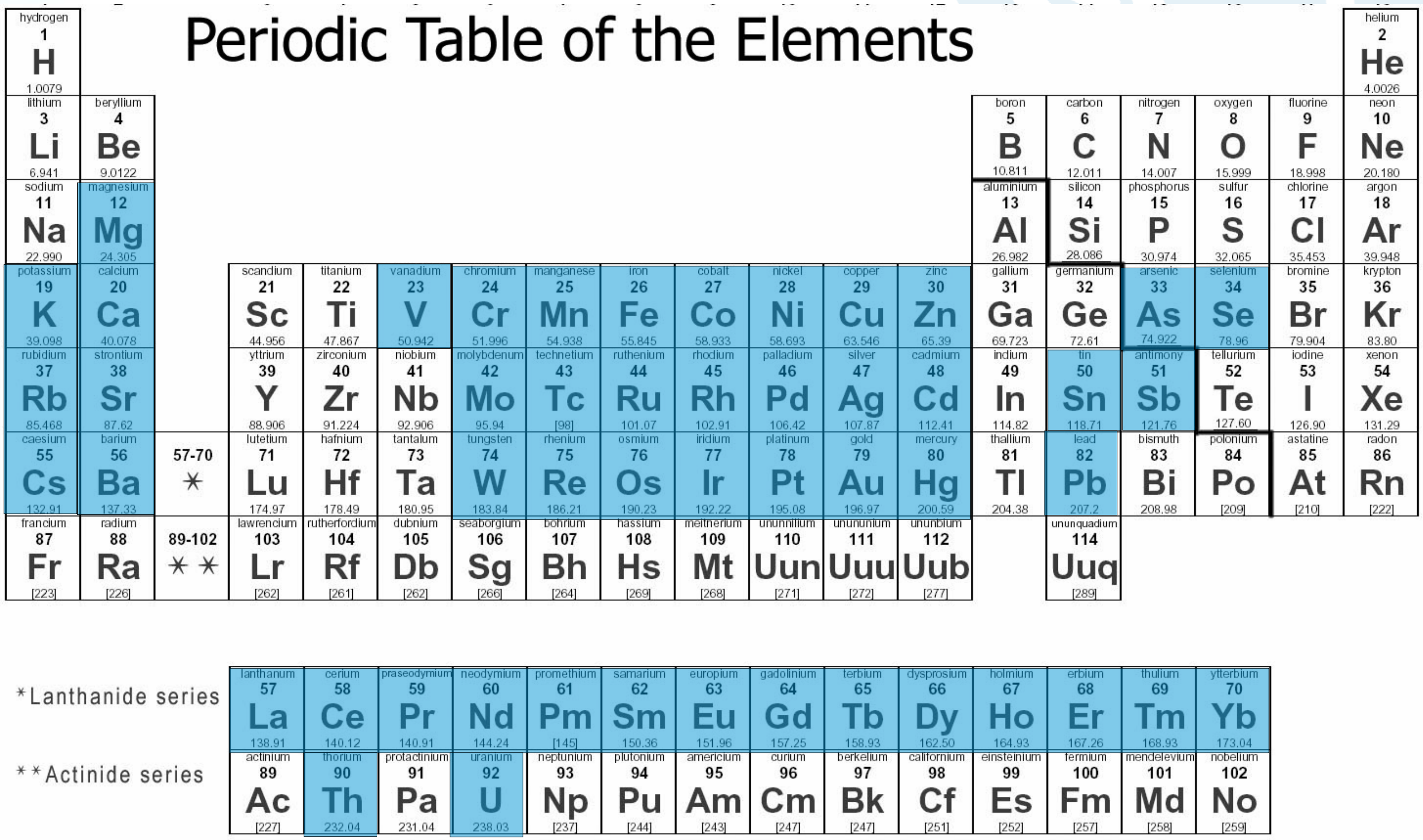
Metals Recovery/Removal



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Biotechnology Applications

- Decolorization of sugar
- Purification of amino acids (cation resins)
- Purification of proteins (cation resins)
- Purification of antibiotics
  - streptomycin (carboxylic acid resins)
  - cephalosporin (medium base anion resin)
  - erythromycin (cation resin)

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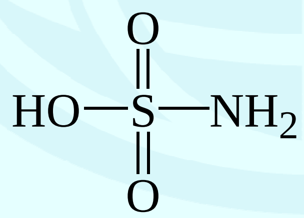
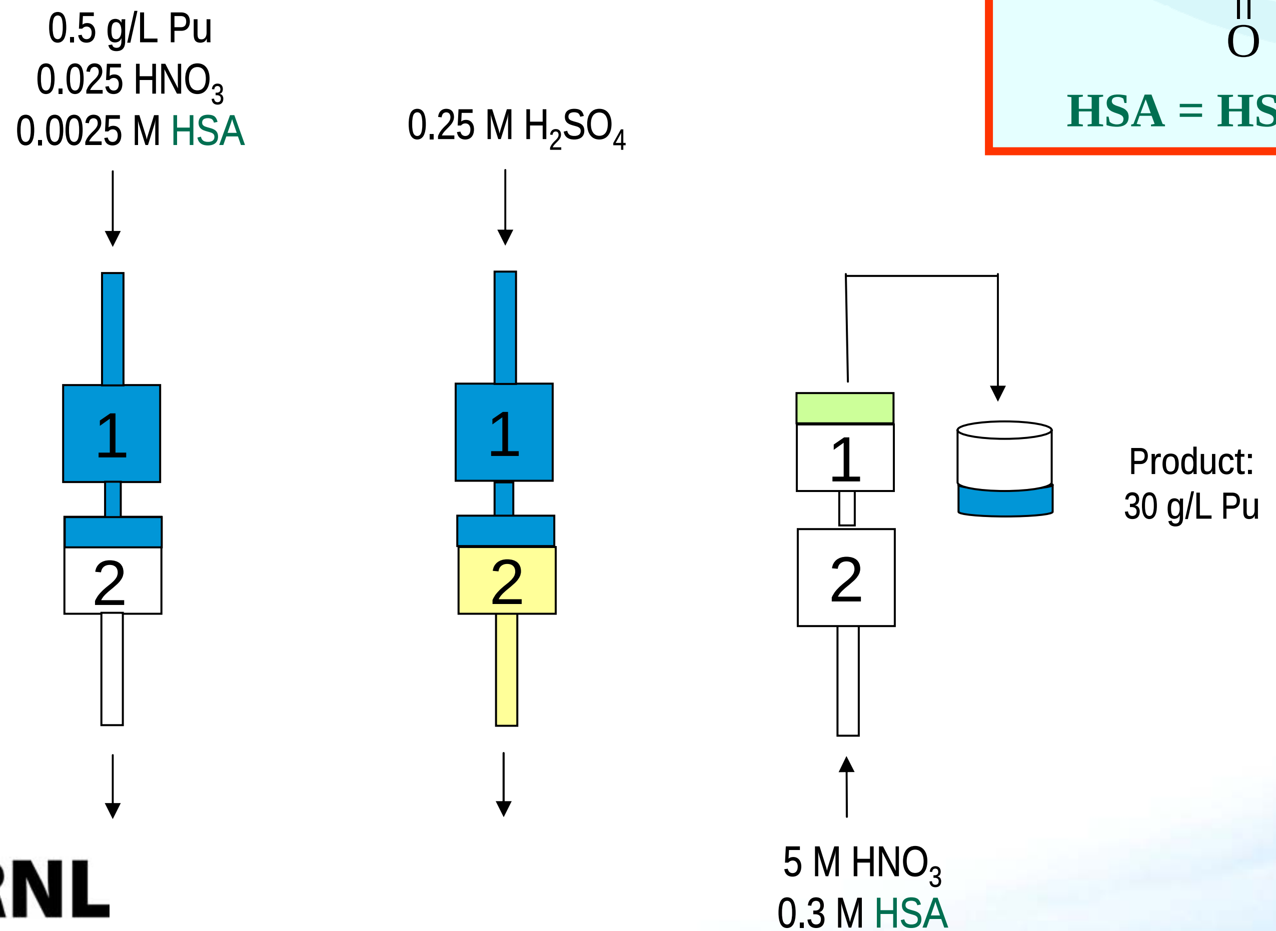
Nuclear Materials Production

- Dilute Pu(III) solution from PUREX process purified and concentrated using cation exchange resin
- Polystyrene-divinylbenzene sulfonic acid (RSO_3H)

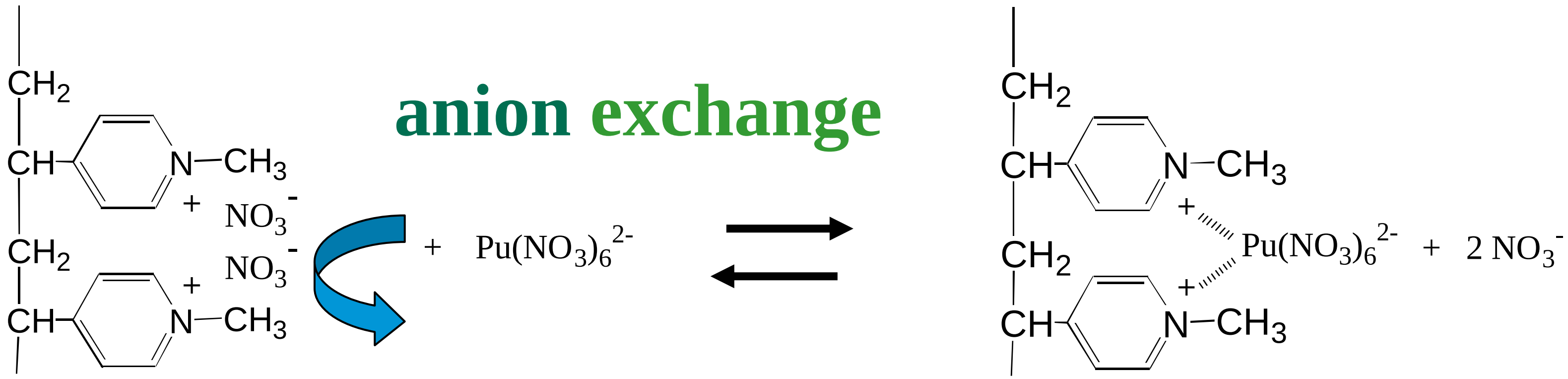


HSA = HSO_3NH_2



Purification of Pu and Np

- Load $Pu(NO_3)_6^{2-}$ or $Np(NO_3)_6^{2-}$ from 8 M HNO_3 onto strong anion exchange resin
- Wash with 6-8 M HNO_3 to remove fission products and impurities
- Elute Pu with 0.3 M HNO_3



Reillex HPQ
anion exchange resin

Ion Exchange Resin Safety

Nitric Acid will oxidize organic resins generating gas and heat

Inadequately vented columns will over pressurize and rupture explosively

Safety Precautions:

- **Keep resin wet at all times**
- **Keep the temperature of the resin below 60 ^{o}C**
- **Keep the ion exchange column vented at all times**
- **Keep the resin radiation exposure level to < 10^8 RAD**
- **Limit Resin Exposure to no more than 9 M HNO_3**
- **Limit Resin Exposure to Oxidizers**

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Cesium Separation from Purex Raffinate

- Purex raffinate concentrated and partially denitrated, made alkaline with NaOH and NH_3, filtered to remove precipitated solids, and filtrate acidified to pH 4 and boiled to remove CO_2
- Ni(II) and ferricyanide added to precipitate $Ni_2Fe(CN)_6$
- $Ni_2Fe(CN)_6 + 2Cs^+ = Cs_2NiFe(CN)_6$
- Add Ag_2CO_3 to metathesize Cs and produce Cs_2CO_3
- >99% recovery
- Process recovered 30,000 Ci ^{137}Cs at Hanford

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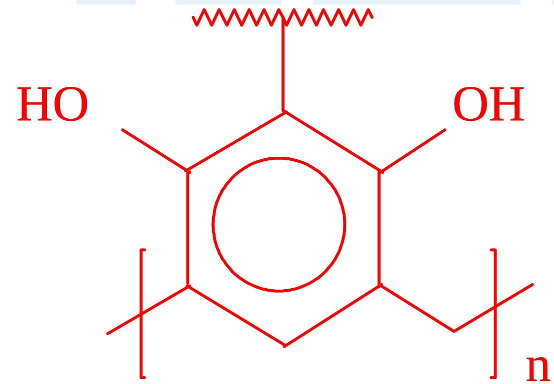
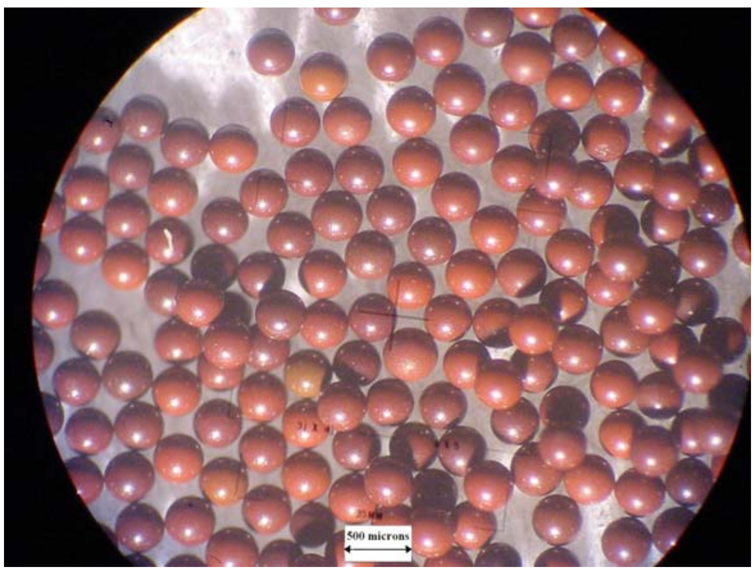
Cleanup of High-Level Wastes

- Cs separation from alkaline waste solutions
- Spherical resorcinol formaldehyde (Microbeads AS)





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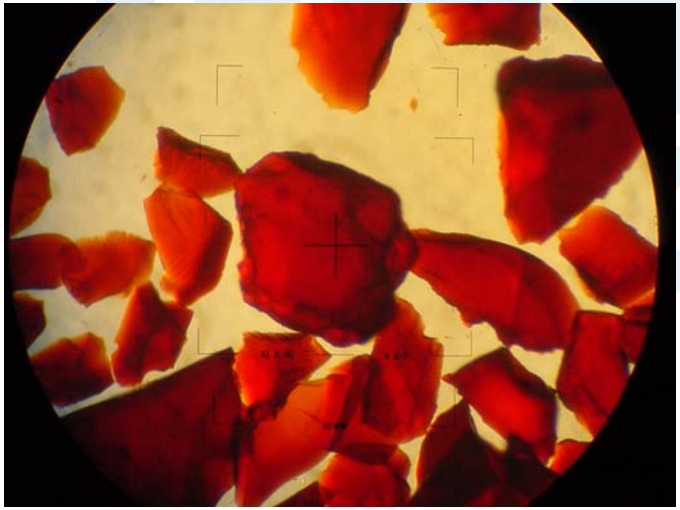
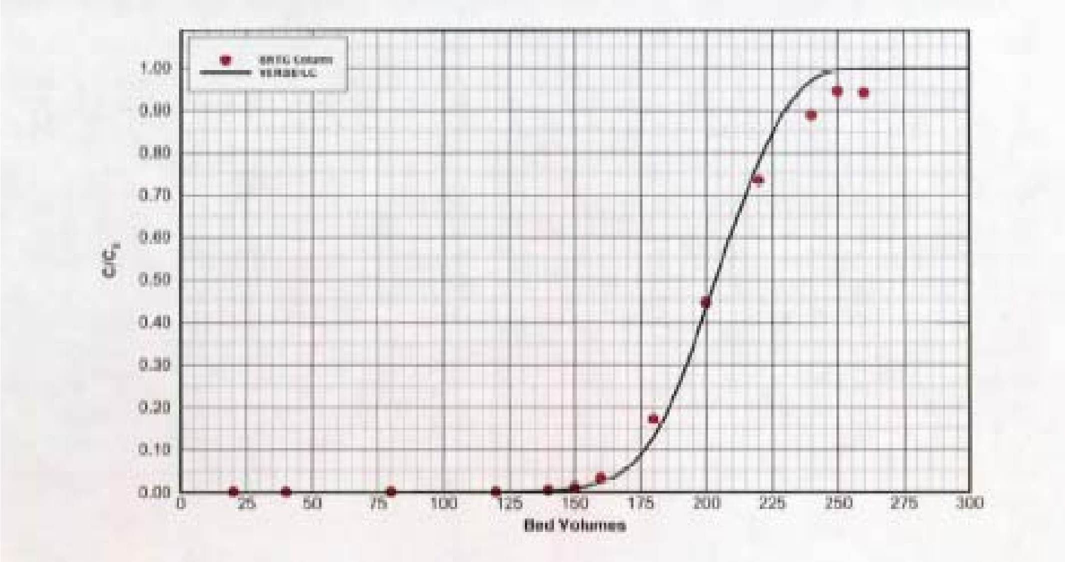
Cleanup of High-Level Wastes

- Cs separation from alkaline waste solutions
- SuperLiq® 644 Resin
  (IBC Advanced Technologies, Inc.)



1. Resin received in H-form
2. Convert to Na-form (1M NaOH)
3. Bed conditioning
   (H_2O, 0.5M HNO_3, H_2O, 0.25M NaOH
4. Bed loading (waste solution)
5. Feed displacement (0.1M NaOH)
6. Elution (0.5M HNO_3)
7. Eluant rinse (DI H_2O)
8. Regeneration (0.25M NaOH)



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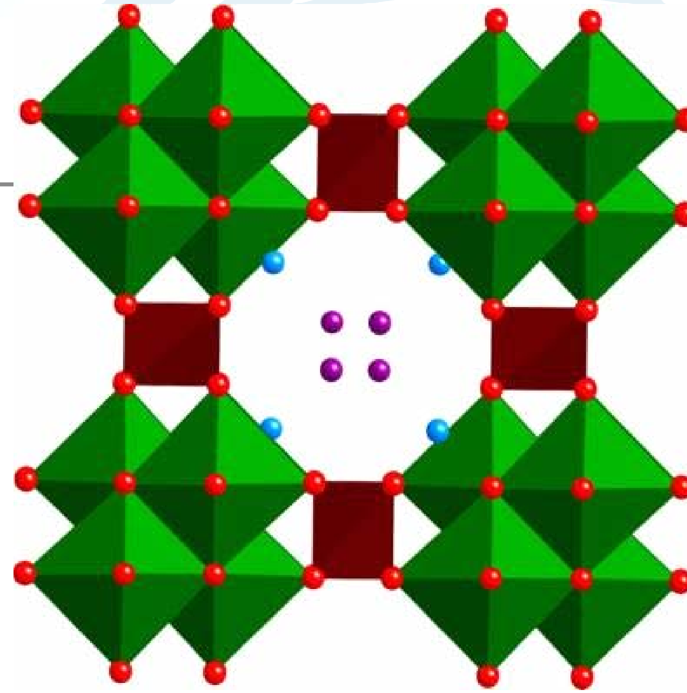
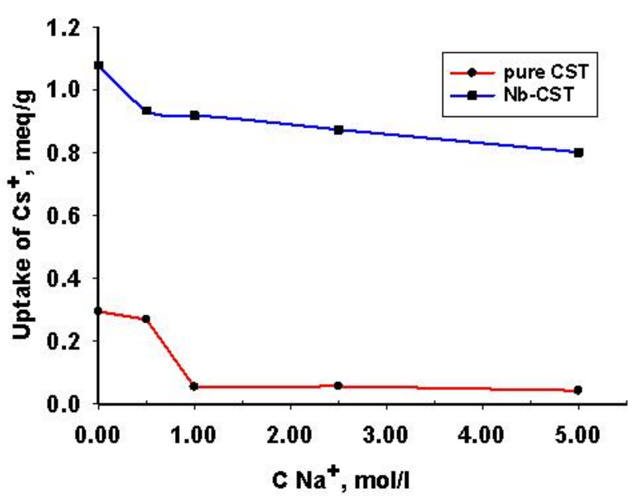
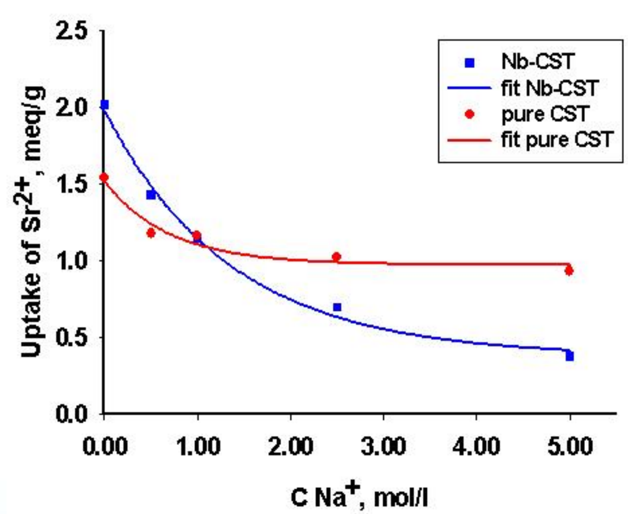
Cleanup of High-Level Wastes



- Crystalline silicotitanate, $Na_2Ti_2O_3(SiO_4)\cdot 2H_2O$ (CST)
- Effective for removing Cs and Sr from alkaline waste solutions
- Partial substitution of Nb for Ti in framework increases selectivity for Cs and decreases selectivity for Sr
- Effectively non-elutable due to phase change between Cs and H-forms
- Commercially available: UOP IE-910 (powder) and IE-911 (engineered)





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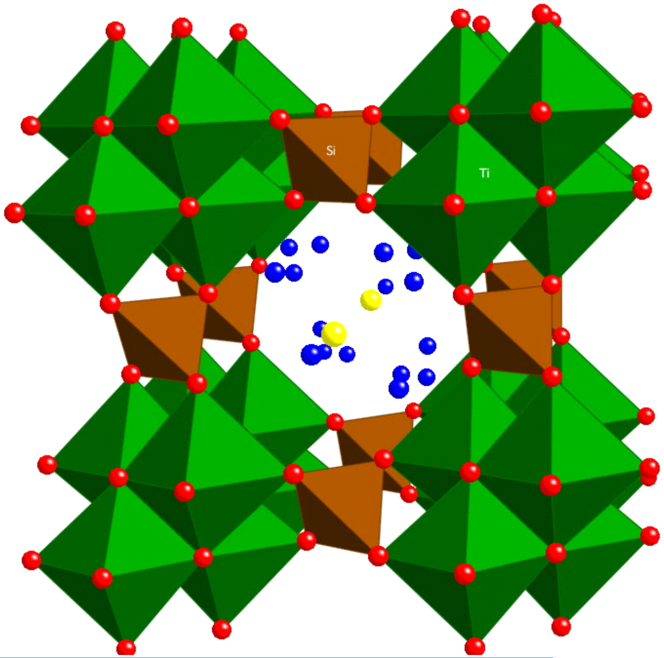
Cleanup of High-Level Wastes

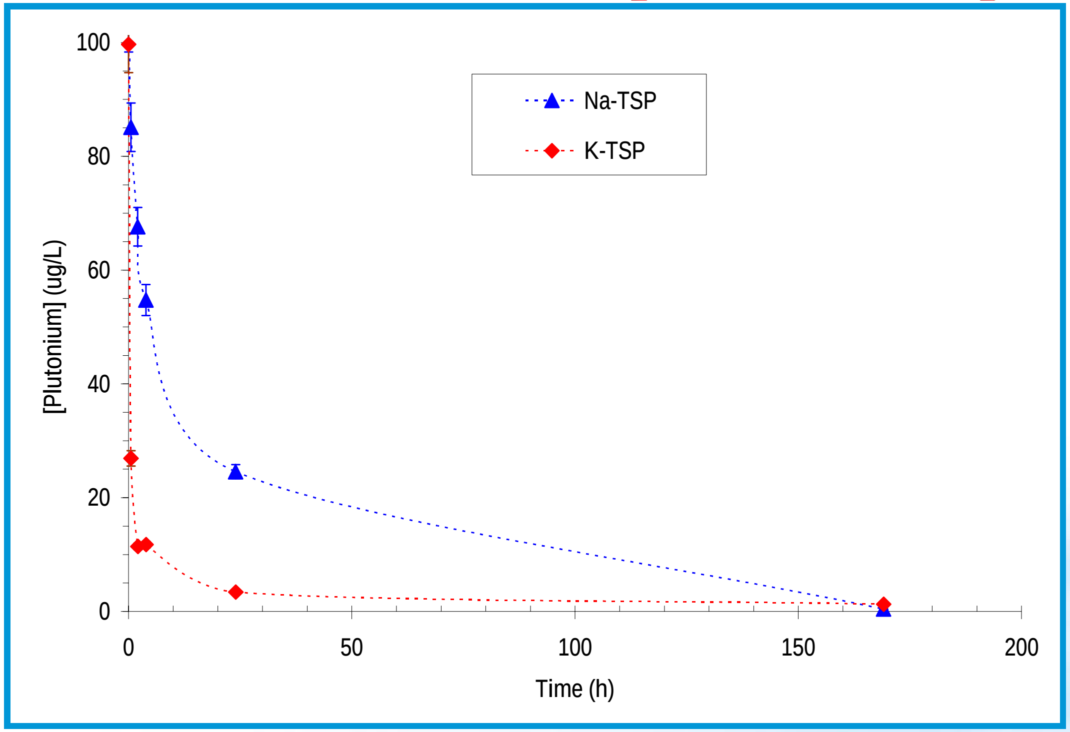
- Titanosilicate, $M_4(TiO)_4(SiO_4)_3 \cdot xH_2O$ (TSP)
  where M = Cs, K, H

- Isostructural to the mineral pharmacosiderite

- H-form exchanges –
  $Cs^+ > K^+ > Na^+ > Li^+$
  $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$

- Na & K-forms exhibit affinity actinides





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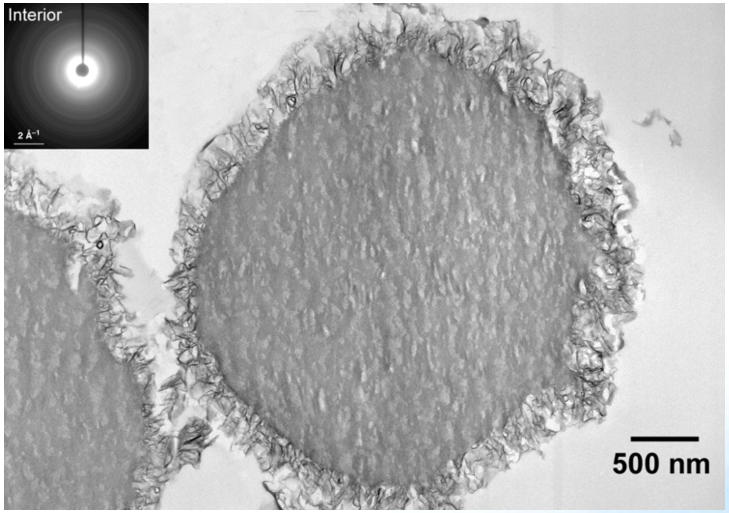
Cleanup of High-Level Wastes

- Monosodium titanate, $NaHTi_2O_5$ (MST)
- Layered amorphous material exhibits high affinity for Sr & actinides over wide range of pH conditions
  - Highly effective in strongly alkaline (>1M free OH^-) and high ionic strength Na solutions (>4.5M in Na)
- Used at SRS – Actinide Removal Process (ARP) and Salt Waste Processing Facility (SWPF)
  - Batch contact process with fine powder
  - Separate solids using ultrafiltration (0.1-micron membrane)

SEM image



TEM image

Conclusions

- Ion exchange processes are a strong commercial market
  - water treatment
  - biotechnology
- Organic-based ion exchange materials dominate the commercial market
- Ion exchange materials successfully used in fuel cycle separations and cleanup of legacy wastes
  - purification of Pu, Np and U
  - separation of fission products and actinides from alkaline wastes

Resources

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